concentrated sulfuric acid in 250 ml. of water. In the first, the above-named components were refluxed for 1 hr. at 60°; in the second, 2-methylfuran was added over a period of 2.5 hr. to the aqueous phenolic acidic solution which was maintained at 60°. In both instances, on work-up, compound IV (confirmed by derivative preparation and also by boiling point) was obtained in *ca.* 50% yield based on the 2-methylfuran charged. Pure phenol recovery was *ca.* 80 and 87%, respectively, the remaining phenol probably being in the aqueous phase and washings. Higher boiling material and tars amounted to *ca.* 13 g. in each case.

5,5-Bis(5-methyl-2-furyl)pentan-2-one (IV).—To a stirred solution of 160 g. (1.65 moles) of concentrated sulfuric acid and 500 g. (28 moles) of water was added 82 g. (1 mole) of 2-methylfuran. The mixture was refluxed for 1 hr. at 60°, cooled, and then transferred to a separatory funnel. The top organic layer (77 g.) was neutralized and then distilled *in vacuo*; 2-methylfuran (10 g., 0.12 mole) was first recovered and then 54 g. (66%) of pale yellow liquid, b.p. 125–128° (1.25 mm.), $n^{25}\text{D}$ 1.5045, leaving a residue of 7 g. On subsequent reuses of the bottom aqueous acidic layer, the yield of the title compound improved and the percentage of 2-methylfuran accounted for approached 100%. Analyses and preparation of derivatives were conducted using a purified sample: b.p. 108° (0.25 mm.); $n^{25}\text{D}$ 1.5050; ν 1715 (vs, carbonyl), 1563 (s)*, 1450 (m), 1362 (s), 1215 (vs), 1156 (m), 1018 (vs, ether), 998 (m), 960 (m), 944 (m), 932 (m), and 782 (vs)* cm.$^{-1}$. The asterisk marks absorbancies reported to be characteristic of 2,5-disubstituted furans,[8,9] the others are consistent with the furan structure.[10-12]

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.36. Found: C, 72.89; H, 7.41.

The bright orange 2,4-dinitrophenylhydrazone,[13] recrystallized from 95% ethanol, melted at 115–116°.

Anal. Calcd. for $C_{21}H_{22}N_4O_6$: C, 59.14; H, 5.20; N, 13.14. Found: C, 59.08; H, 5.13; N, 12.83.

The white semicarbazone,[13] m.p. 162–163°, was recrystallized from 50% ethanol.

Anal. Calcd. for $C_{16}H_{21}N_3O_3$: C, 63.34; H, 6.98; N, 13.85. Found: C, 63.35; H, 6.96; N, 13.67.

The hydantoin[14] was obtained as a white powder after recrystallization from 50% ethanol and melted at 131.5–132.5°.

Anal. Calcd. for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86. Found: C, 64.38; H, 6.46; N, 8.82.

5,5-Bis(2-furyl)pentan-2-one (V).—This compound was prepared by refluxing 25 g. (0.17 mole) of 4-oxopentanal dimethylal, 102 g. (1.5 moles) of furan, and 30 g. of 85% phosphoric acid dissolved in 6.5 ml. of water in 300 ml. of benzene for about 6 hr. Neutralization of the reaction mixture, followed by distillation *in vacuo* of the benzene layer, gave the crude material: b.p. 90–96° (0.23 mm.); ν 1720 (vs, carbonyl), 1595 (m), 1505 (vs), 1415 (m), 1362 (vs), 1231 (s), 1150 (vs), 1074 (m)*, 1008 (vs, ether), 942 (s), 922 (m), 909 (m), 883 (s)*, 805 (s)*, and 735 (vs)* cm.$^{-1}$. The asterisk marks absorbancies reported to be characteristic of 2-substituted furans[8-10]; the others are consistent with the furan structure.[11,12]

The orange 2,4-dinitrophenylhydrazone[13] was recrystallized from 95% ethanol and melted at 104–106°.

Anal. Calcd. for $C_{19}H_{18}N_4O_6$: C, 57.28; H, 4.55; N, 14.07. Found: C, 57.42; H, 4.68; N, 14.04.

The colorless semicarbazone,[13] after recrystallization from 50% ethanol, melted at 166–167°.

Anal. Calcd. for $C_{14}H_{17}N_3O_3$: C, 61.07; H, 6.23; N, 15.26. Found: C, 61.13; H, 6.13; N, 15.21.

---

(8) M. Fetizon and J. Guy, *Compt. rend.*, **247**, 1182 (1958); *Chem. Abstr.*, **54**, 70*d* (1960).

(9) K. Takano, *Nippon Kagaku Zasshi*, **82**, 373 (1961); *Chem. Abstr.*, **56**, 10071*d* (1962).

(10) E. Mantica, R. Ercoli, and L. P. Bicelli, *Rend. ist. lombardo sci., Pt. I*, **91**, 802 (1957); *Chem. Abstr.*, **53**, 3881*e* (1959).

(11) A. H. J. Cross, S. G. E. Stevens, and T. H. E. Watts, *J. Appl. Chem.* (London), **7**, 562 (1957); *Chem. Abstr.*, **52**, 4323*b* (1958).

(12) L. Daasch, *Chem. Ind.* (London), 1113 (1958); *Chem. Abstr.*, **53**, 3882*a* (1959).

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 170–171.

(14) H. R. Henze and R. J. Speer, *J. Am. Chem. Soc.*, **64**, 522 (1942).

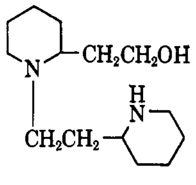
Hydrogenation in the Pyridine Series. III. Formation of a By-product in the Nickel-Catalyzed Reduction of 2-(2-Hydroxyethyl)pyridine

Morris Freifelder, Yew Hay Ng, and George R. Stone

Organic Chemistry Department, Research Division,
Abbott Laboratories, North Chicago, Illinois

Received December 23, 1964

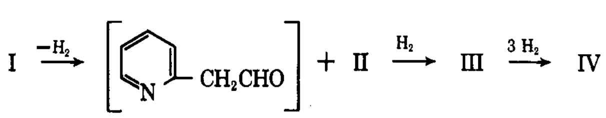
Prior to the investigation of the use of rhodium and ruthenium catalysts in the hydrogenation of pyridines,[1] 2-(2-hydroxyethyl)pyridine (I) was reduced in the presence of Raney nickel at 150° and 130 atm. for 8–15 hr. In addition to 2-(2-hydroxyethyl)piperidine (II), a much higher boiling material was obtained. From elemental analysis a formula of $C_{14}H_{28}N_2O$ was derived. Near-infrared and infrared examinations showed the presence of NH and OH and the absence of the pyridine ring. Structure IV seemed to fit the data on hand.



IV

The structure was corroborated by treating 2-vinylpyridine with II to give 1-[2-(2-pyridyl)ethyl]-2-(2-hydroxyethyl)piperidine (III), which was subsequently hydrogenated at low pressure in the presence of rhodium on a carrier. The resultant product compared in all respects with IV obtained from the high-pressure nickel reduction of I.

The formation of IV from II may have taken place in the following manner.[2] We have been able to



obtain 5–10% yields of IV by treating I and II under high-pressure hydrogenation conditions with Raney nickel. In the reaction of II alone, under similar conditions, over 60% of it was recovered unchanged. In addition, about 25% of 2-methylpiperidine was obtained.[3]

Compound IV could also form by dehydration of I to 2-vinylpyridine which, in turn, would follow the series of reactions which was used to corroborate the

---

(1) M. Freifelder, R. M. Robinson, and G. R. Stone, *J. Org. Chem.*, **27**, 284 (1962); M. Freifelder and G. R. Stone, *ibid.*, **26**, 3805 (1961).

(2) The phenomenon of catalytic dehydrogenation of alcohols and subsequent reductive alkylation of amines with the resultant aldehyde has been pointed out by R. G. Rice and E. J. Kohn [*J. Am. Chem. Soc.*, **77**, 4052 (1955)]. The formation of carbonyl compound resulting from such dehydrogenation has been reported by B. B. Corson and H. Dressler [*J. Org. Chem.*, **21**, 474 (1956)].

(3) M. G. Reinecke and L. R. Kray [*ibid.*, **29**, 1737 (1964)] point out that dehydroxymethylation is the primary process occurring during attempted cyclization of II; E. R. Lavagnino, R. R. Chauvette, W. N. Cannon, and E. C. Kornfeld [*J. Am. Chem. Soc.*, **82**, 2609 (1960)] report dehydroxymethylation to 2-methylpiperidine on heating II in water with a large amount of Raney nickel.

structure of IV. Such a scheme seemed less likely to us. Our expectation that 2-vinylpyridine would be reduced too rapidly to 2-ethylpyridine and subsequently to 2-ethylpiperidine to allow III to form was confirmed when it was hydrogenated in the presence of II at 150° and 130 atm. with Raney nickel. 2-Ethylpiperidine was obtained in over 80% yield. Additional material boiling slightly higher than 2-ethylpiperidine (possibly contaminated with 2-ethylpyridine) raised the consumption of 2-vinylpyridine to 97%. Seventy per cent of II was recovered.

Experimental[4]

1-[2-(2-Piperidyl)ethyl]-2-(2-hydroxyethyl)piperidine (IV).—A solution of 87.0 g. (0.7 mole) of 2-(2-hydroxyethyl)pyridine in 150 ml. of absolute ethyl alcohol was hydrogenated at 150° and 130 atm. in the presence of 12.0 g. of commercial Raney nickel. Uptake of hydrogen was usually complete in 8–15 hr. After removal of the catalyst and distillation of the solvent, the residue was fractionated. After collection of the fraction boiling at 85–87° (0.3 mm.), which gave an unsatisfactory analysis for 2-(2-hydroxyethyl)piperidine,[5] the remaining portion was collected at 142–156° (0.3 mm.): $n^{25}\text{D}$ 1.4977, 8% yield. The material solidified and was recrystallized from hexane: m.p. 92–96°, $\lambda_{\max}^{\text{CCl}_4}$ 1.42 (OH) and 1.55 μ (NH), $\lambda_{\max}^{\text{CHCl}_3}$ no pyridine bands.

Anal. Calcd. for $C_{14}H_{28}N_2O$: C, 69.95; H, 11.74; N, 11.66. Found: C, 70.29; H, 11.78; N, 11.95.

Proof of Structure of IV. Preparation of III.—Following a recently described procedure,[6] a solution of 103.2 g. (0.8 mole) of 2-(2-hydroxyethyl)piperidine, 42.0 g. (0.4 mole) of freshly distilled 2-vinylpyridine, 150 ml. of methyl alcohol, and 12.0 g. (0.2 mole) of glacial acetic acid was heated in a 1-l. stainless steel rocker-type bomb for 24 hr. at 65–70°. The reaction mixture was concentrated and the residue was dissolved in water and treated with excess 50% sodium hydroxide solution. The oily layer which separated was dissolved in ether and the remainder of the solution was extracted several more times. After drying the extract over anhydrous magnesium sulfate, removal of the drying agent, and distillation of solvent, the residue was fractionated. After recovery of excess 2-(2-hydroxyethyl)-piperidine, 1-[2-(2-pyridyl)ethyl]-2-(2-hydroxyethyl)piperidine (III) was obtained in 34% yield: b.p. 175–178° (2.4–2.5 mm.); $n^{25}\text{D}$ 1.5307; $\lambda_{\max}^{\text{film}}$ 3.05 (broad, OH), 6.27, 6.36, and 6.78 μ (pyridine).

Anal. Calcd. for $C_{14}H_{22}N_2O$: C, 71.75; H, 9.47; N, 11.95. Found: C, 71.47; H, 9.82; N, 11.90.

Hydrogenation of III to IV.—A solution of 23.4 g. (0.1 mole) of III in 100 ml. of ethyl alcohol was hydrogenated at 60° and 3 atm. in the presence of 10 g. of 5% rhodium on alumina. Uptake of hydrogen was complete before reaction temperature was reached (0.5 hr.). The solution was filtered from the catalyst which was washed with additional alcohol. After removal of the solvent under reduced pressure, the residue solidified on treatment with hexane and seeding with a crystal of known product. The material was treated with cold hexane and filtered. A yield of almost 92% of IV was obtained melting at 95–97°, not depressed when mixed with known material. It was analyzed without further purification.

Anal. Calcd. for $C_{14}H_{28}N_2O$: C, 69.95; H, 11.74; N, 11.66. Found: C, 69.81; H, 11.61; N, 11.61.

Reduction of I in the Presence of II.—A mixture of 61.5 g. (0.5 mole) of 2-(2-hydroxyethyl)pyridine and 64.5 g. (0.5 mole) of 2-(2-hydroxyethyl)piperidine was hydrogenated at 160° and 120 atm. in the presence of 13–15 g. of Raney nickel. At the end of 5 hr. 3 equiv. of hydrogen were absorbed. When the reaction mixture was cool, it was filtered and the catalyst was rinsed with ethyl alcohol. The solvent was concentrated under reduced pressure and the residue was then fractionated. After collection of 53 g. of II, a higher boiling fraction, b.p. 197° (4.3 mm.), was collected, yield 6%. It solidified and melted at 91°. Its infrared spectrum was identical with IV.

The remaining material which solidified in the distillation flask was dissolved in 200 ml. of anhydrous ether and treated with alcoholic hydrogen chloride until the mixture was acidic. On standing, a sticky mass formed. Decanting the solvent and treating the material with dry acetone made it filterable. It was then recrystallized by dissolving in hot absolute alcohol and adding the solution to several volumes of anhydrous ether. It was identified as the dihydrochloride salt of IV: m.p. 150° with preliminary softening; 2% yield.

Anal. Calcd. for $C_{14}H_{30}Cl_2N_2O$: C, 53.66; H, 9.65; Cl, 22.63; N, 8.95. Found: C, 53.59; H, 10.02; Cl, 22.65; N, 9.10.

Hydrogenation of a Mixture of 2-Vinylpyridine and II.—A solution of 0.4 mole of II and 0.4 mole of freshly distilled 2-vinylpyridine in 125 ml. of ethyl alcohol was treated with hydrogen at 150° and 120-atm. pressure in the presence of 20 g. of Raney nickel. Uptake of hydrogen started at 100°; at 160°, uptake was about 3.5 equiv., indicative of conversion of 2-vinylpyridine to 2-ethylpiperidine. Reaction was continued for several hours. After cooling and removal of the catalyst, the solution was distilled through a packed column. The alcohol which was collected was strongly basic. It was treated with alcoholic hydrogen chloride until acidic and concentrated to dryness. The dried salt (22.0 g.) melted at 182°. The melting point was not depressed when mixed with an authentic sample of 2-ethylpiperidine hydrochloride. More 2-ethylpiperidine as base was collected at 135–140° (atmospheric pressure): $n^{25}\text{D}$ 1.4469. The total yield of pure material was 86%. Two slightly higher boiling fractions, b.p. 70° (50 mm.), $n^{25}\text{D}$ 1.4474, and b.p. 79° (36 mm.), $n^{25}\text{D}$ 1.4484, weighing a total of 8.0 g. were also obtained. From the boiling points, *ca.* 150° and 160° at atmospheric pressure, and the refractive indices they appeared to be 2-ethylpiperidine contaminated with some 2-ethylpyridine. This raised the yield of 2-ethylpiperidine to 97%. About 35.0 g. of II was recovered (70%).

Effect of Hydrogenation Conditions on II.—A solution of 51.6 g. (0.4 mole) of II in 250 ml. of ethyl alcohol was heated and rocked in a 1-l. stainless steel bomb for 3 hr. at 150° and 120 atm. in the presence of 10–15 g. of Raney nickel. After cooling and removal of catalyst, the solution was distilled at atmospheric pressure. The alcohol which was collected was basic. It was neutralized with alcoholic hydrogen chloride and concentrated to dryness. A salt, 3 g., was obtained; m.p. 210°. The next fraction (8.0 g.) distilled at 115–120° (described for 2-methylpiperidine, 119°). It was converted to the hydrochloride salt, m.p. 210°, not depressed on mixing with a known sample. The total yield of 2-methylpiperidine was about 25%. Close to 70% of II was recovered: b.p. 128° (20 mm.), $n^{25}\text{D}$ 1.4842.

---

[4] Melting points were taken on Fisher-Johns apparatus and are not corrected. Microanalyses were carried out by Mr. O. F. Kolsto and his group, infrared and near-infrared spectra by A. Kammer and W. Washburn.

[5] From the consistently high carbon values it appeared that the fraction was likely a mixture of II and the 1-ethyl derivative of II resulting from reduction conditions in the presence of alcohol: M. Freifelder, *Advan. Catalysis*, **14**, 206 (1963).

[6] G. M. Singerman and R. Levine, *J. Heterocyclic Chem.*, **1**, 151 (1964), method A.

The Claisen Rearrangement of Resorcinol Monoallyl Ether

KURT D. KAUFMAN AND WILLIAM E. RUSSEY

Department of Chemistry, Kalamazoo College, Kalamazoo, Michigan

Received December 7, 1964

It has been reported[1] that resorcinol monoallyl ether (Ia) rearranges to 4-allylresorcinol (II) at temperatures between 170 and 280°. Nesmejanow and Sarewitsch[1b] obtained a crystalline sample of II, m.p. 67°, although Hurd, *et al.*,[1a,c] were unable to isolate any crystalline products from the rearrangement. None of the previous workers reported 2-allylresorcinol (III) as a product of the rearrangement.

---

[1] (a) C. D. Hurd, H. Greengard, and F. D. Pilgrim, *J. Am. Chem. Soc.*, **52**, 1700 (1930); (b) A. N. Nesmejanow and T. S. Sarewitsch, *Ber.*, **68**, 1476 (1935); (c) C. D. Hurd and M. P. Puterbaugh, *J. Org. Chem.*, **2**, 381 (1937).